

Large Bipolaron in a Polaron-Gas Background

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Abstract

A criterion, proposed by the present authors, is used to derive numerical results for the stability of a large bipolaron embedded in a polaron gas. The main conclusion is that an isolated metastable bipolaron can be stabilized by the polaron gas surroundings because of the Fermi statistics of polarons. On the other hand, it is found that the exchange interaction tends to destabilize the bipolaron. The study is performed both for bulk (3D) materials and for thin (2D) films within the Hartree-Fock approximation. The bipolaron is described by an extension of the Feynman polaron model.

Two electrons (or holes) in a polar crystal interact with the phonon field which may lead to their binding into a composite quasi-particle, a *bipolaron*. The binding into a bipolaron results if the attraction between the electrons, due to the virtual phonon exchange, is sufficiently strong to overcome the electron-electron repulsion.

In this letter we deal with the so called large (bi)polarons (e.g. Refs. [3–5]; for more references see the review articles [6,7]). The singlet large bipolaron is characterized by two dimensionless coupling constants. The first one, the Fröhlich coupling constant

$$\alpha = \frac{1}{\hbar\omega_{\text{LO}}} \frac{e^2}{\sqrt{2}} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \sqrt{\frac{m_b\omega_{\text{LO}}}{\hbar}} \quad (1)$$

is a measure of the strength of the electron-phonon interaction while the second one

$$U = \frac{1}{\hbar\omega_{\text{LO}}} \frac{e^2}{\varepsilon_{\infty}} \sqrt{\frac{m_b\omega_{\text{LO}}}{\hbar}} \quad (2)$$

is the Coulomb potential coupling constant which governs the strength of the direct electron-electron repulsion. In (1) and (2) ε_0 and ε_{∞} are the static and the high-frequency dielectric constants, m_b is the electron band mass and ω_{LO} is the frequency of the longitudinal optical (LO) phonons. Introducing the ratio of the dielectric constants $\eta = \varepsilon_{\infty}/\varepsilon_0$, one obtains the following relation between the Coulomb and the electron-phonon coupling constants $U = \sqrt{2}\alpha/(1 - \eta)$. As $\eta \geq 0$, only values $U \geq \sqrt{2}\alpha$ have a physical meaning. In what follows use is also made of the parameter

$$u = \frac{U}{\sqrt{2}\alpha} = \frac{1}{1 - \eta} . \quad (3)$$

The physical relevant region is then defined by the inequality $u \geq 1$.

To find the stability region of the bipolaron in the (α, u) -plane one usually exploits the following condition

$$E_{bip} \leq 2E_{pol}, \quad (4)$$

where E_{pol} and E_{bip} denote the ground state energies of the polaron and the bipolaron at rest, respectively. This inequality implies that the decay of the bipolaron into two polarons

is not energetically advantageous. With (4) the bipolaron turns out to be stable if α is larger than some critical coupling constant α_c . In three dimensions (3D) the following estimates have been reported for the critical value of the electron-phonon coupling constant: $\alpha_c = 7.3$ in Ref. [4], $\alpha_c = 6.8$ in Ref. [3] and $\alpha_c = 6$ in Ref. [5]. Even if α exceeds the critical value α_c , the possibility of large bipolaron formation depends on the strength of the direct Coulomb repulsion which tends to prevent electrons to congregate into a cluster. Namely, E_{bip} obeys (4) at $\eta \leq \eta_c(\alpha)$ (or, equivalently, $u \leq u_c(\alpha)$). For example, for large coupling, $\alpha = 9$, it has been found that $\eta_c \approx 0.056$ ($u_c \approx 1.059$) in Ref. [4] and $\eta_c \approx 0.037$ ($u_c \approx 1.038$) in Ref. [3]. (The quoted results for α_c and η_c , u_c leave little hope that the 3D singlet large bipolaron can survive even in special kinds of materials (such as strongly ionic crystals)).

In reality, the inequality (4) is the stability criterion for an *isolated bipolaron*; it is not applicable for a bipolaron interacting with a system of charge carriers. In Ref. [8] the present authors have proposed a stability criterion for a 3D bipolaron embedded in a polaron gas. The basic idea is the following. Polarons are fermions and obey the Pauli principle. Therefore the two polarons in a final state after the bipolaron decay must have their momenta outside the Fermi-surface. Consequently, the total kinetic energy of two such final state polarons cannot be less than $2(p_F^2/2m_{pol})$ where m_{pol} is the polaron effective mass. We must add this term to the r.h.s of the criterion (4). This evidently makes the bipolaron decay less probable. That is, the bipolaron is possibly stabilized because of the Fermi statistics of the final state polarons. Furthermore, the polaron-polaron and the bipolaron-polaron interactions should be taken into account.

In the present letter we restrict ourselves to the Hartree-Fock approximation and perform the calculations for an arbitrary number D of dimensions to obtain the following formulae for the 2D bipolaron. The D -dimensional Fermi-momentum is given by the expression

$$p_F = 2\sqrt{\pi}\hbar \left[\frac{n}{2} \Gamma(1 + D/2) \right]^{1/D}, \quad (5)$$

where $n = N/V$ is the polaron concentration in a D -dimensional box. In the Hartree-Fock approximation the mean kinetic energy per particle (without polaron effects) reads as follows

$$W(n) = \langle \frac{p^2}{2m_{pol}} \rangle = \frac{2\pi\hbar^2}{m_{pol}} \frac{D}{D+2} \left[\frac{n}{2} \Gamma(1 + D/2) \right]^{2/D} = \frac{D}{D+2} \frac{p_F^2}{2m_{pol}}. \quad (6)$$

A term to be added to the r.h.s of the criterion (4) is the difference between the kinetic energies of $N+2$ polarons (after the bipolaron decay) and that of N polarons (the bipolaron is assumed to be at rest):

$$\begin{aligned} \Delta_{kin} &= (N+2) \left\langle \frac{p^2}{2m_{pol}} \right\rangle \Big|_{N+2} - N \left\langle \frac{p^2}{2m_{pol}} \right\rangle \Big|_N \\ &= V \left[\left(n + \frac{2}{V} \right) W \left(n + \frac{2}{V} \right) - n W(n) \right] = 2 \frac{\partial}{\partial n} [nW(n)] \\ &= \frac{4\pi\hbar^2}{m_{pol}} \left[\frac{n}{2} \Gamma(1 + D/2) \right]^{2/D} = 2 \frac{p_F^2}{2m_{pol}}. \end{aligned} \quad (7)$$

Thus, Δ_{kin} is twice the polaron kinetic energy on a Fermi-surface.

In a similar way we treat the potential energy of the polaron gas. At large distances $r \gg r_{pol}$ (where r_{pol} is the polaron radius) the polaron-polaron and the bipolaron-polaron interactions can be approximated by Coulomb potentials screened by the static dielectric constant: $\Phi_{pp} \sim e^2/\varepsilon_0 r$ and $\Phi_{bp} \sim 2e^2/\varepsilon_0 r$. In the Hartree-Fock approximation the exchange energy per particle is then approximated as follows

$$\Pi(n) = -\frac{\pi e^2}{\varepsilon_0 n} \frac{\Gamma\left(\frac{D-1}{2}\right)}{(2\pi^{3/2}\hbar)^{D+1}} \int_{|\vec{k}|, |\vec{q}| \leq p_F} \frac{d^D \vec{k} d^D \vec{q}}{|\vec{k} - \vec{q}|^{D-1}}. \quad (8)$$

The integral in (8) can be evaluated

$$\int_{|\vec{k}|, |\vec{q}| \leq p_F} \frac{d^D \vec{k} d^D \vec{q}}{|\vec{k} - \vec{q}|^{D-1}} = p_F^{D+1} \frac{4\pi^{(D-1/2)}}{\Gamma(D/2)\Gamma[(D+3)/2]}, \quad (9)$$

and we obtain from Eq. (8)

$$\Pi(n) = -\frac{e^2}{\varepsilon_0} \frac{4D}{\sqrt{\pi}(D^2-1)} \left[\frac{n}{2} \Gamma(1 + D/2) \right]^{1/D}. \quad (10)$$

The exchange energy to be added to the r.h.s of the criterion (4) takes therefore the form

$$\Delta_{exc} = 2 \frac{\partial}{\partial n} [n\Pi(n)] = -\frac{e^2}{\varepsilon_0} \frac{8}{\sqrt{\pi}(D-1)} \left[\frac{n}{2} \Gamma(1 + D/2) \right]^{1/D} = -\frac{e^2}{\varepsilon_0} \frac{4}{\pi(D-1)} \frac{p_F}{\hbar}. \quad (11)$$

Finally, in the Hartree-Fock approximation, we arrive at the following *in-medium* criterion for the bipolaron stability

$$E_{bip} - 2E_{pol} \leq \frac{p_F^2}{m_{pol}} - \frac{e^2}{\varepsilon_0} \frac{4}{\pi(D-1)} \frac{p_F}{\hbar}. \quad (12)$$

The r.h.s. of (12) is equal to zero for $p_F = 0$ and for $p_F = p_d$, where p_d is given by the relation

$$p_d = \frac{m_{pol} e^2}{\hbar \varepsilon_0} \frac{4}{\pi(D-1)}. \quad (13)$$

In the interval $0 < p_F < p_d$, that is at small polaron concentrations, the r.h.s. of the criterion (12) is negative which allows the bipolaron to decay even if it is stable when isolated. In this case the exchange energy dominates and a “stable” bipolaron (in the sense of the criterion (4)) is destabilized by the polaron gas. In the interval $p_F > p_d$ the effect of the Fermi statistics dominates and the r.h.s. of (12) is positive thus additionally stabilizing the bipolaron in comparison with what follows from (4).

At $D = 3$ we arrive at the stability criterion [8]

$$E_{bip} - 2E_{pol} \leq \frac{\hbar^2}{m_{pol}} (3\pi^2 n)^{2/3} - 2 \frac{e^2}{\varepsilon_0} \left(\frac{3n}{\pi} \right)^{1/3}. \quad (14)$$

In dimensionless units the criterion (14) takes the form

$$\frac{E_{bip} - 2E_{pol}}{\hbar \omega_{LO}} \leq \frac{m_b}{m_{pol}} \left(3\pi^2 \frac{n}{n_0} \right)^{2/3} - 2\sqrt{2}(u-1) \alpha \left(\frac{3}{\pi} \frac{n}{n_0} \right)^{1/3}. \quad (15)$$

Here n_0 denotes the natural unit for the polaron concentration

$$n_0 = \left(\frac{m_b \omega_{LO}}{\hbar} \right)^{3/2}. \quad (16)$$

Its typical value can be estimated with the data of Ref. [9]. For instance, for RbCl $m_b = 0.432m_e$ (m_e is the electron mass) and $\omega_{LO} = 3.4 \cdot 10^{13} \text{ s}^{-1}$, so $n_0 \sim 4.5 \cdot 10^{19} \text{ cm}^{-3}$.

For quasi-particles confined to a two-dimensional ($D = 2$) layer (12) takes the form

$$E_{bip} - 2E_{pol} \leq \frac{\hbar^2}{m_{pol}} 2\pi\sigma - 4 \frac{e^2}{\varepsilon_0} \sqrt{\frac{2\sigma}{\pi}}, \quad (17)$$

where we used the notation σ for the surface concentration of polarons. Eq. (17) can be written as follows

$$\begin{aligned} \frac{E_{bip} - 2E_{pol}}{\hbar\omega_{LO}} &\leq \frac{m_b}{m_{pol}} 2\pi \frac{\sigma}{\sigma_0} - 8(u-1)\alpha \sqrt{\frac{\sigma}{\pi\sigma_0}}, \\ \sigma_0 &= \frac{m_b\omega_{LO}}{\hbar} = n_0^{2/3}. \end{aligned} \quad (18)$$

We used the criteria (14), (15) in Ref. [8] to study the possibility of stabilizing the bipolaron, restricting ourselves to the limiting case $u = 1$ (that is, omitting the exchange energy which diminishes the bipolaron stability region). The goal of the present letter is to study both stabilization and destabilization effects in more detail using the criteria (15), (18). To calculate the bipolaron and the polaron ground state energies use is made of the bipolaron model of Ref. [3] which is a generalization of the Feynman model for the single polaron. As for any Gaussian approximation, the results for the polaron ground state energy and the effective mass in different dimensions are linked to each other by a scaling relation introduced in Ref. [10],

$$E_{pol}^{(2D)}(\alpha) = \frac{2}{3} E_{pol}^{(3D)}\left(\frac{3\pi}{4}\alpha\right), \quad m_{pol}^{(2D)}(\alpha) = m_{pol}^{(3D)}\left(\frac{3\pi}{4}\alpha\right). \quad (19)$$

A similar scaling relation is valid for the bipolaron energy [3] (the Coulomb coupling constant is not scaled). At the “destabilizing” concentration n_d corresponding to the value p_d of Eq. (13), the r.h.s. of the stability criterion equals zero. The bipolaron energy then equals twice the polaron energy. This occurs at the boundary of the bipolaron stability region found with the old criterion (4). In 3D we obtain n_d from (15)

$$\frac{n_d}{n_0} = \frac{16\sqrt{2}}{3\pi^5} \left[\frac{m_{pol}}{m_b} \alpha (u_c(\alpha) - 1) \right]^3 \quad (20)$$

and in 2D from (18)

$$\frac{\sigma_d}{\sigma_0} = \frac{16}{\pi^3} \left[\frac{m_{pol}}{m_b} \alpha (u_c(\alpha) - 1) \right]^2. \quad (21)$$

To find a simple estimate for n_d we may use the interpolation formula derived in Ref. [12] for the bipolaron model used here in 3D:

$$u_c(\alpha) = 1.08525 \frac{\alpha^2 - 10.925}{\alpha^2 - 7.969} \quad (22)$$

(note that u of the present letter differs by a factor $\sqrt{2}$ from u of the paper [12]). Inserting Eq. (22) into Eq. (20) and using the value of the polaron mass calculated in the scope of the Feynman model, we may estimate n_d . For instance, at $\alpha = 7$ we obtain $m_{pol}/m_b = 14.4$ and $n_d = 0.01n_0$. The strong dependence of n_d on α is mostly due to the strong dependence of m_{pol} on it. That is, the smaller is α the less is the bipolaron destabilization effect.

The interpolation formula for $u_c(\alpha)$ in 2D can be found with the same scaling law (19): $u_c^{(2D)}(\alpha) = u_c^{(3D)}(3\alpha/4\pi)$. It follows then for the 2D case

$$u_c(\alpha) = 1.08525 \frac{\alpha^2 - 1.968}{\alpha^2 - 1.435}. \quad (23)$$

Because of the scaling relations the value $\alpha = 4 \times 9/3\pi = 3.82$ in 2D produces the same polaronic effects as $\alpha = 9$ in 3D. For this α the polaron mass takes the value $m_{pol}/m_b = 62.7$ and Eq. (21) gives the surface concentration $\sigma_d \approx 50\sigma_0$. The numerical solution leads at the value $\sigma_d \approx 43\sigma_0$. For $\alpha = 2.97$ in 2D, which corresponds to $\alpha = 7$ in 3D, we obtain $\sigma_d \approx 0.04\sigma_0$.

This means that the bipolaron which is stable when isolated can decay into two polarons for concentrations $n < n_d$ ($\sigma < \sigma_d$). In the opposite case $n > n_d$ ($\sigma > \sigma_d$) our in-medium stability criterion allows the bipolaron to exist even if its energy exceeds twice the polaron energy. Such a bipolaron being isolated would decay, therefore we call it a metastable bipolaron. For a given value of α a metastable bipolaron is seen in the range of the Coulomb coupling constant $u_c(\alpha) \leq u \leq u_{max}(\alpha)$. Only a state of two free polarons was seen at $u > u_{max}(\alpha)$.

In Fig. 1 the bipolaron ground state energy is shown as a function of the Coulomb coupling constant u for $\alpha = 9$ in 3D. Subsequently, the same curve is obtained in 2D for $\alpha = 4 \times 9/(3\pi) = 3.82$ (cf. the right y -axis). In this case the isolated bipolaron is stable for $1 \leq u \leq u_c = 1.038$. In the region $u_c \leq u \leq u_{max} = 1.146$ the bipolaron energy exceeds twice the polaron energy but this metastable state can be stabilized by the polaron gas. At $u \geq u_{max}$ our numerical program has found only two separate polarons minimum.

In Fig. 2 regions are shown where polarons, bipolarons and metastable bipolaron states exist. The top x -axis corresponds to the 2D case. The metastable bipolaron is seen to occur for $\alpha \geq \alpha_{min} \approx 6.5$ (in 3D) which is slightly smaller than the critical value $\alpha_c \approx 6.8$. Note also that a metastable bipolaron was also reported in Ref. [11].

It follows from our stability criterion that the metastable bipolaron is stabilized by the polaron environment for concentrations $n > n_d$. The stabilizing effect is evident for α close to the critical value (we choose $\alpha = 7$ for the 3D case in Fig. 3): the limiting value of the Coulomb coupling constant increases with the polaron concentration n . Bipolarons can exist for the parameter values below the plotted curve. The stability region of the isolated bipolaron is determined by $u \leq u_c$. At $n = n_{lim} \approx 2.4n_0$ the constant u reaches its maximal value u_{max} . Note that typical concentrations for stability of bipolarons $n_d \sim 10^{18} \div 10^{19} \text{ cm}^{-3}$ are close to charge-carrier concentrations of heavily doped degenerate polar semiconductors [13–15].

The similar plot for $\alpha = 3.82$ in 2D is presented in Fig. 4. Both the stabilization (at $\sigma > \sigma_d \approx 43\sigma_0$) and the destabilization (at $\sigma < \sigma_d$) effects are seen clearly.

To conclude, we have formulated an in-medium stability criterion for bipolarons which takes into account Fermi statistics and the exchange energy. The former stabilize the bipolaron while the latter destabilizes it. The competition of these two effects depends on the polaron concentration. Our treatment of the bipolaron is variational and therefore it is not to be excluded that some of the relative minima found here for the bipolaron energy as a function of variational parameters are artefacts of the method.

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FIGURES

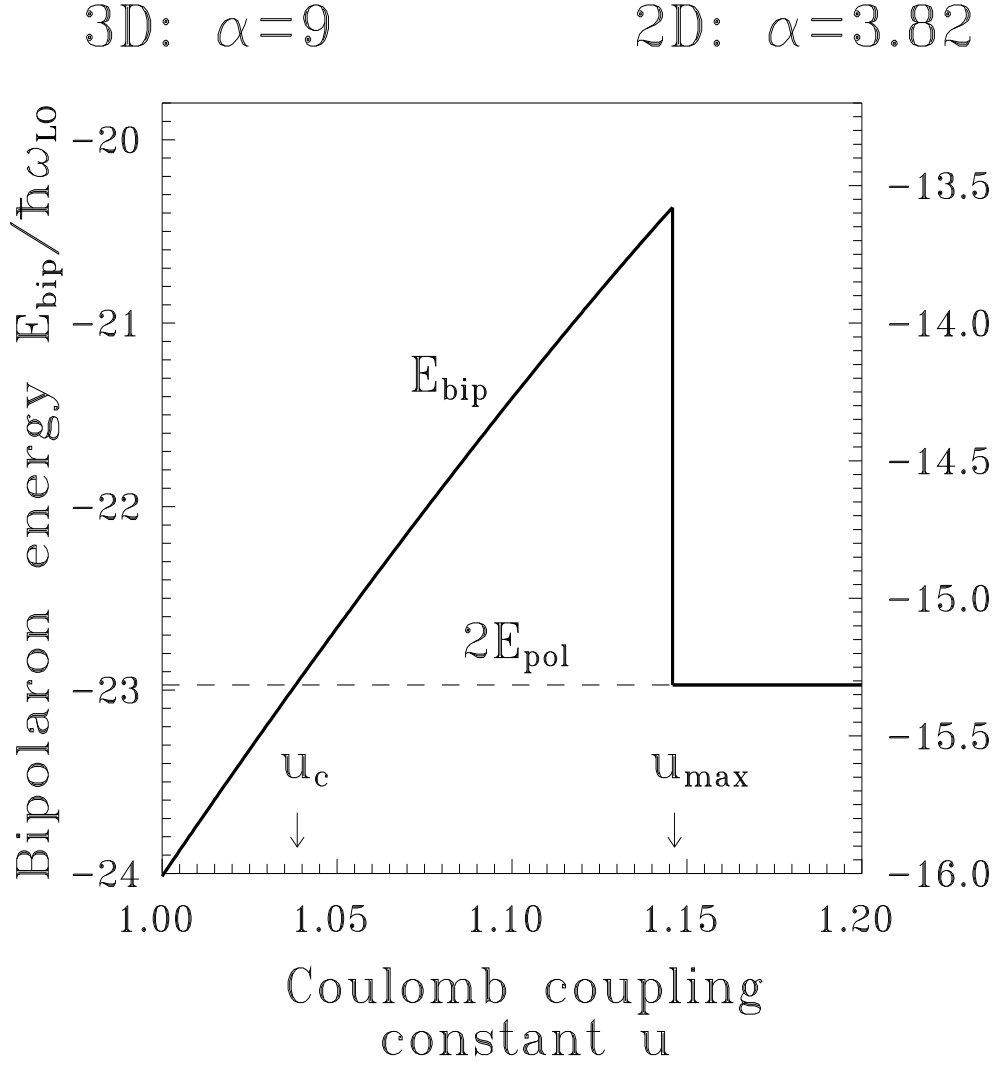


FIG. 1. The metastable bipolaron energy vs. the Coulomb coupling constant at $\alpha = 9$ (in 3D) and $\alpha = 3.82$ (in 2D).

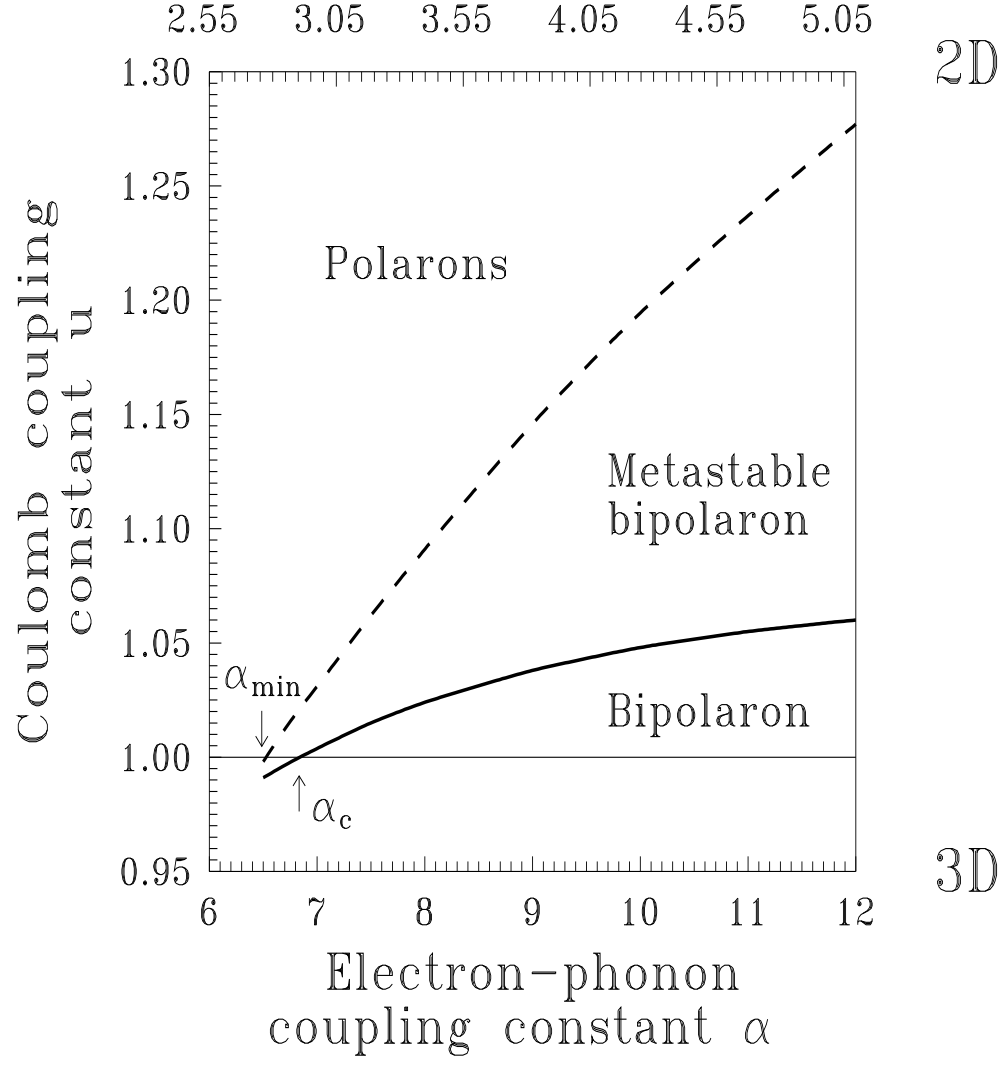


FIG. 2. “Phase” diagram in the plane of the coupling constants (u, α) .

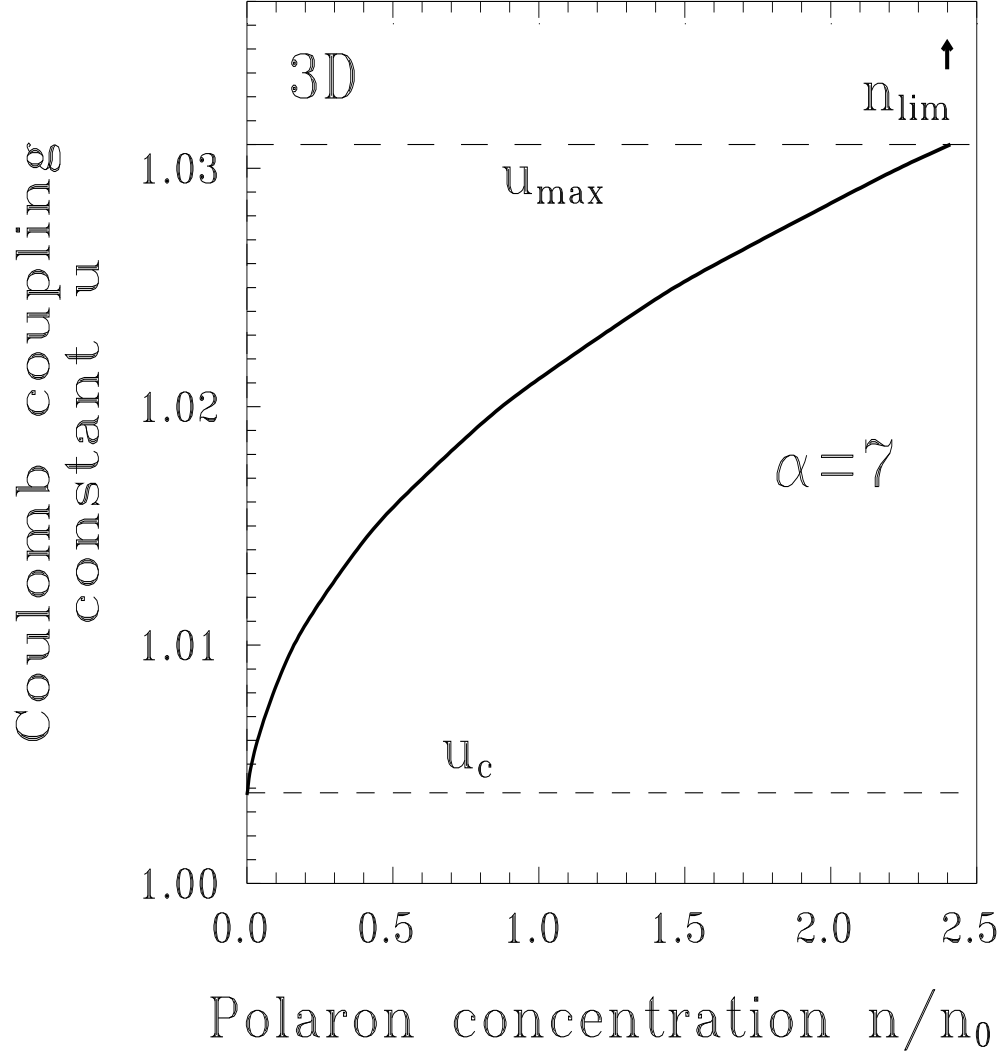


FIG. 3. The limiting value of the Coulomb coupling constant u vs. the polaron concentration for $\alpha = 7$. The 3D metastable bipolaron is stabilized by the polaron environment in the region below the shown curve. The destabilization effect is negligible in this case.

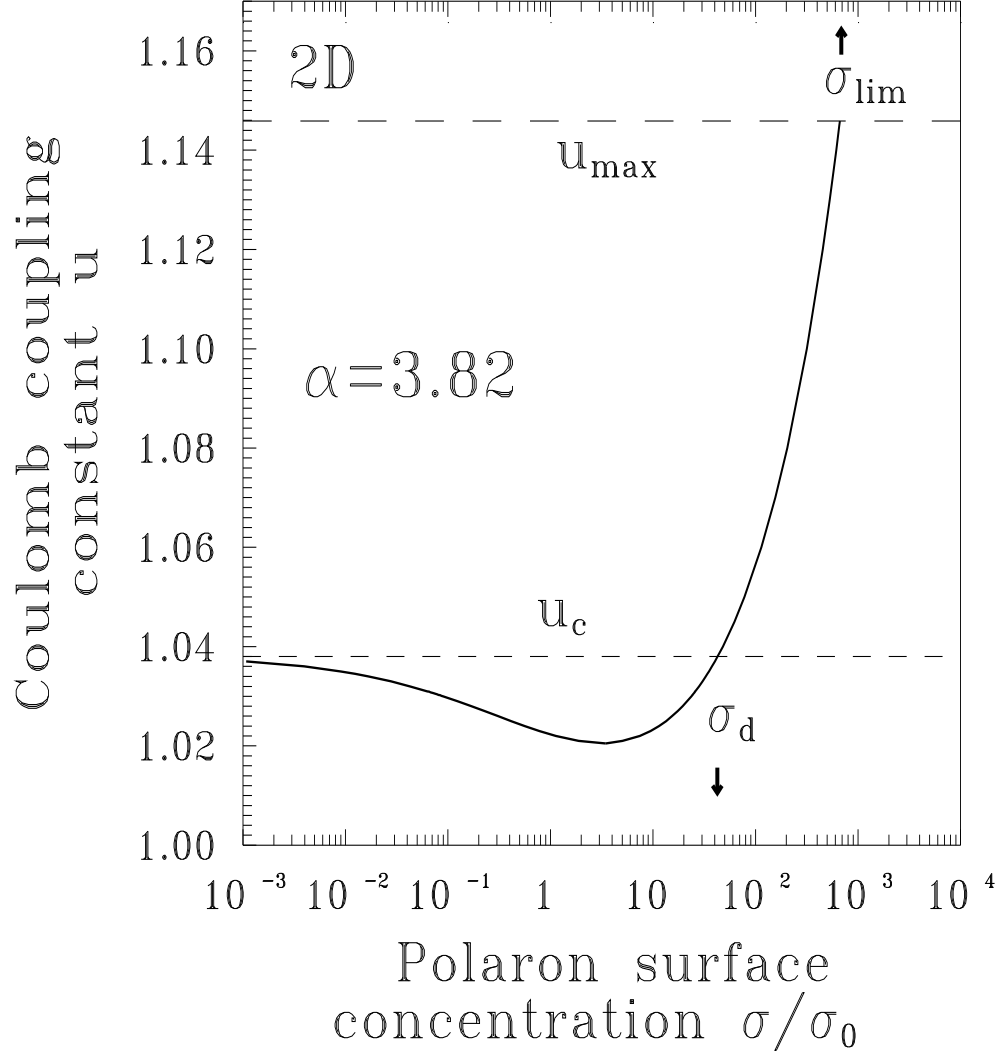


FIG. 4. The limiting value of the Coulomb coupling constant u vs. the polaron surface concentration for $\alpha = 3.82$. The 2D metastable bipolaron is stabilized by the polaron environment in the region below the shown curve at $\sigma > \sigma_d \approx 43\sigma_0$. The destabilization of the bipolaron happens for the concentrations $0 < \sigma < \sigma_d$.